The coil-globule transition of polymers of long rigid monomers connected by flexible spacers

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A simple model of a polymer with long rigid segments which interact via excluded volume repulsions and short ranged attractions is proposed. The coil–globule transition of this model polymer is strongly first order, the globule is crystalline and the coil which coexists with the globule is swollen. A virial expansion truncated at low order is shown to provide a very poor approximation to the free energy and so a cell theory is used to calculate the free energy of the globule.

I. INTRODUCTION

Typically, in a dilute polymer solution, each polymer chain is spread over a very large volume.[1] The polymer chain forms a fractal and if a box is drawn so as to enclose the chain, almost all of the volume within the box is occupied by solvent, not by the monomers of the polymer. This is the coil state of a polymer chain. The coil may be ideal, in which case its radius of gyration scales with the number of its monomers N as $N^{1/2}$, or it may be swollen, in which case its radius of gyration scales as $N^{3/5}$. The value $3/5$ of the exponent is the Flory value,[1] the true value is slightly less.[6] However, there is a second state of the polymer: the globular state, in which the radius of gyration scales as $N^{1/3}$. As the radius of gyration scales with $N^{1/3}$, the volume scales linearly with N, the density is then finite (except at a second order transition to the coil state). The volume occupied by a coil increases more rapidly than linearly with N and so as N becomes very large the density tends to zero. The state of a polymer is in turn determined by the interactions between different parts of the polymer. If they repel each other then the polymer is the swollen coil state, if they attract each other strongly enough then the polymer is in the globular state, whilst if the attractive and repulsive parts of the interactions balance the polymer is ideal apart from logarithmic corrections.[1,6] By decreasing the temperature and so increasing the effect of the attractive forces the polymer may be transformed from a coil to a globule. A considerable amount of theoretical work has been devoted to attempting to understand and describe the coil–globule transition. However, this has concentrated almost exclusively on coil–globule transitions driven by the polymer's second virial coefficient becoming negative.[2–9] In the coil state, the interaction part of the free energy is dominated by interactions between only two parts of the polymer, which are accounted for by the polymer chain's second virial coefficient (which is general different from the second virial coefficient of the monomers). So, as the second virial coefficient decreases to zero the interactions effectively vanish and the coil becomes (almost) ideal. Then on reducing the temperature further the second virial coefficient becomes negative and the coil collapses into a globule. The coil first becomes ideal before collapsing only when the collapse is driven by the change of sign of the polymer's second virial coefficient. Here, we show that when the monomers are long and rigid the coil–globule transition is not driven by the second virial coefficient becoming negative. So, the polymer is *never* ideal. When the temperature is reduced the polymer transforms via a strongly first order transition from a swollen coil to a dense crystalline globule.

The use of a virial expansion[10] in order to describe the contribution of monomer–monomer interactions to the free energy of the polymer is reasonable for spherical monomers with not too short ranged attractive interactions. However, if the monomers are long and rigid an additional length scale, the length of the monomer L, is present. Unless the range of the attraction is as long or longer than this length L then the attractive forces between the monomers are highly anisotropic.[11–13] Then, their effect on the third and higher virial coefficients is larger than on the second virial coefficient.[13] Long rigid monomers behave in a similar way to hard spheres with a short ranged attraction.[14–18]. Stell[14,15] has shown that, as the range of attraction between the spheres tends to zero, the virial expansion becomes pathological at temperatures such that the attractive interactions make a nonnegligible contribution to the second virial coefficient. Here, we show that the same occurs for long rods as the range of attraction goes to zero. Unless the renormalisation required[1] on going from the virial coefficients of the monomers to the effective virial coefficients of a polymer completely changes the behaviour of the virial series, the coil–globule transition cannot be driven by the renormalised second virial coefficient becoming negative.

The DNA double helix is a rather rigid polymer, its persistence length[19] is ~ 50nm[20] which is 25 times its diameter of ~ 2nm. The interaction between DNA helices has a much shorter range than 50nm[20–23] and so we would expect the behaviour of a DNA molecule of length $\gg 50$nm, to be qualitatively similar to that of our model polymer chain. This expectation is borne out, the coil–globule transition of DNA, as for our model, is first order.[8,9,24]

II. THE MODEL POLYMER CHAIN

The polymer is a linear chain of N cylindrical monomers joined with $(N-1)$ flexible spacers, see Fig. (1). A spacer is flexible enough to allow the two cylinders which it joins to adopt any relative orientation with equal probability and to lie side-by-side, however, its maximum length is much less that the length L of a cylindrical monomer. We will always consider N to be infinite and so the coil–globule transition is a phase transition. Real polymers are, of course, always finite but we do not consider the effect of finite size here.

The cylindrical monomers are of length L, and have a hard core of diameter D; when two cylinders overlap the energy of interaction is positive and infinite. The attractive part of the potential is sticky in the sense that its range is close to zero, it is only nonzero between a pair of cylinders if they almost touch for all of their length, for this to be true they must be almost parallel and their centres of mass must be almost side-by-side, i.e., only a little more than D apart. We will define what we mean by almost below when we define the potential. When the attractive part of the potential is nonzero it equals $-\epsilon$. The interaction u between two cylinders, 1 and 2, is a function of the separation $\mathbf{r}_{12}$ of the centres of mass of the cylinders, and of the angle γ_{12} between the centrelines of the two cylinders. Then, $u(\mathbf{r}_{12}, \gamma_{12})$ is defined by

$$\begin{array}{llll} \text{if} & D < r_{12} < (1+\delta)D, \quad |z_{12}| < \delta D, \quad \gamma_{12} < \delta & & u = -\epsilon \\ \text{else if the hard cores overlap} & & & u = \infty \\ \text{otherwise} & & & u = 0, \end{array} \tag{1}$$

where the vector $\mathbf{r}_{12} = (r_{12}, z_{12}, \phi_{12})$ in cylindrical polar coordinates. The origin of the coordinates is fixed on the centre of mass of cylinder 1 and their z-axis is along its axis. The parameter $\delta \ll 1$ defines how far apart the cylinders can be and still interact via the attractive part of their interactions. The limit $\delta \to 0$ defines a zero range potential, a generalisation to a cylinder of the sticky sphere potential of Baxter.[14,25] The dependences of the attractive part of the potential u on γ_{12} and on the components of $\mathbf{r}_{12}$ are independent; this is rather artificial but allows a simple evaluation of the second virial coefficient and as δ is near zero the details of the attractive interaction make little difference to the behaviour of the polymer.

In Eq. (1), δ and ϵ are just adjustable parameters. However, for an attractive interaction of range $\sim D$ between rods of length L the energy of interaction of two parallel rods scales linearly with L/D.[13,21] This produces a very deep well, or a large ϵ in terms of our model. The energy continues to scale linearly with L/D as long as the angle between the two rods is $\lesssim D/L$. Thus, the $L/D \to \infty$ limit of the potential models considered by van der Schoot and Odijk[13] is very similar to the $\epsilon \to \infty$, $\delta \to 0$ and $\epsilon\delta \to$ constant limit of Eq. (1).

III. THE COIL STATE

The density of a coil tends to zero as N tends to infinity. Thus, the only interactions between distant parts of the chain that count are pair interactions; the density is so low that the probability of three different parts of the chain coming close enough to interact is vanishingly small.[1,6] By distant parts of the chain we mean monomers which are not close together along the chain, i.e., are separated along the chain by many other monomers. As only pair interactions are important the excess free energy depends on only one parameter, an effective second virial coefficient B_2^r. This is not the same as the second virial coefficient between monomers, B_2. The effective coefficient B_2^r is obtained by renormalising B_2; this 'mixes in' some of the higher virial coefficients in with B_2 to produce B_2^r. So, we start by determining B_2 and then go on to estimate the higher virial coefficients.

In the limit of the temperature tending to infinity, the polymer chain is just a chain of hard cylinders and flexible spacers.[26] Then, $B_2 = (\pi/4)L^2 D$.[19,27] The higher virial coefficients are all very small if $L/D \gg 1$.[19,27] Thus interactions between pairs of the monomers are close to being independent, and so if two distant (along the chain) monomers are interacting the probability of any of the monomers which are adjacent to either of these monomers interacting with either of the original pair of monomers is very low. As it is these interactions which renormalise B_2, we conclude that the renormalisation required to derive B_2^r from B_2 is weak and so $B_2^r \simeq B_2$. The pair interactions cause the coil to swell so that its radius of gyration scales as $N^{3/5}$, not as $N^{1/2}$ as an ideal coil does. However, they contribute an amount much less than T to the free energy per monomer. T is the temperature in energy units. This can be seen if we examine the interactions between distant and between adjacent monomers. The interaction between distant pairs of monomers, i.e., pairs of monomers which are not neighbours or next-nearest neighbours etc. along the chain, is characterised by the Fixman parameter[1,6,28] $z \sim B_2/L^3 N^{1/2}$. If we divide this by N to obtain the contribution per monomer we see that the contribution tends to zero as N tends to infinity. As for the interaction between adjacent monomers; it is easy to see that a monomer only very weakly restricts the space available to an adjacent monomer. Thus, the contribution to the free energy from interactions between monomers is small. Then the free energy of our

chain is to a good approximation the free energy of an ideal chain. If the flexible spacers allow each monomer to move freely in a phase space of volume D^3 then the free energy per monomer of the coil a is

$$a(T) = -T \ln D^3. \tag{2}$$

Of course there is also a term from the momenta but we neglect this as it is the same in all phases. Fixing the volume of phase space to be D^3 is consistent with short tethers of length not much larger than D.

In order to consider the effect of attractive interactions we start by studying the second and third virial coefficients of sticky cylinders. In fact the contribution of pairwise interactions to the free energy of a coil involves not B_2 but a renormalised second virial coefficient B_2^r.[1] The difference between the two will be considered after the unrenormalised coefficients have been calculated. The second virial coefficient is[10,19]

$$B_2(T) = -\frac{1}{32\pi^2} \int \left(\exp[-u(\mathbf{r}_{12}, \gamma_{12})/T] - 1 \right) d\mathbf{r}_{12} d\Omega_1 d\Omega_2, \tag{3}$$

where $d\Omega_i = \sin\theta_i d\theta_i d\phi_i$. The diagrammatic representation of B_2 is given by Fig. (2a). See Ref. 10 for an introduction to the theory of diagrams. The integral in Eq. (3) is straightforward. For $\gamma > \delta$ the interaction is just that between two hard rods, whose B_2 is well known.[19,27] The contribution of the attractive part of the interaction is evaluated by aligning cylinder 1 with the z-axis, then $\gamma_{12} = \theta_2$, and as the integration is restricted to small angles $\sin\theta_2 \simeq \theta_2$. So,

$$B_2(T) = \frac{\pi}{4}L^2D - \frac{1}{4}\exp[\epsilon/T]\int_D^{D+\delta D} 2\pi r_{12}dr_{12} \int_{-\delta D}^{\delta D} dz_{12} \int_0^\delta \theta_2 d\theta_2, \tag{4}$$

where cylindrical polar coordinates have been used for $\mathbf{r}_{12}$. We have assumed that $L/D \gg 1$ and $\epsilon/T \gg 1$.

$$B_2(T) = \frac{\pi}{4}L^2D - \frac{\pi}{2}D^3\delta^4 \exp[\epsilon/T]. \tag{5}$$

This expression for B_2 may be compared with those derived by van der Schoot and Odijk[13] for more realistic potentials. If in Eq. (5), δ is replaced by D/L and ϵ multiplied by L/D, then it becomes essentially the same as Eq. (3.7) of Ref. 13.

The twelfth virial coefficient of sticky spheres diverges to minus infinity at all temperatures at which the attractive interactions make a nonnegligible contribution to the second virial coefficient.[14] Here, we show that the third virial coefficient B_3 of sticky cylinders diverges to minus infinity at all temperatures for which the attractive interactions make a nonnegligible contribution to B_2, in the limit that δ tends to zero. B_3 is defined by[10]

$$B_3(T) = -\frac{1}{384\pi^3} \int \prod_{ij=12,13,23} \left(\exp[-u(\mathbf{r}_{ij}, \gamma_{ij})/T] - 1 \right) d\mathbf{r}_{12} d\mathbf{r}_{13} d\Omega_1 d\Omega_2 d\Omega_3, \tag{6}$$

where $\mathbf{r}_{13}$ is the vector between the centres of mass of rods 1 and 3, and where γ_{13} and γ_{23} are the angles between rods 1 and 3, and 2 and 3, respectively. The diagrammatic representation of B_3 is given by Fig. (2b). Only the scaling of B_3 with ϵ and δ is required, it is

$$B_3(T) \sim L^3D^3 - D^6\delta^9 \exp[3\epsilon/T]. \tag{7}$$

The first term is from the hard core.[19,27] There are three interactions between the three rods, this gives the factor of 3 in the exponential of the second term of Eq. (7). The integration over the interaction of the first rod with each of the the second and third rods gives a factor of δ^4, then as the rods are already restricted to be nearly parallel and the second and third rods are already restricted to being close to the first rod the integration over the interaction between the second and third rods gives only a factor of δ. In the limit of $\delta \to 0$ the second term of B_2, Eq. (5), is finite if ϵ diverges as $\epsilon \to \ln\delta^{-4}$. Then the attractive interactions contribute a finite amount to the value of B_2. Putting this dependence of ϵ into Eq. (7) results in the attractive term in B_3 tending to minus infinity as $\delta \to 0$. The divergence of the twelfth virial coefficient of sticky hard spheres is suppressed by the presence of even very weak polydispersity in the diameter of the spheres. In contrast, polydispersity in the diameter D of sticky rods has little effect: B_3 still diverges.

Although we cannot consider all virial coefficients we are able to find a trend in their behaviour. The fourth virial coefficient B_4 is the sum of the 3 diagrams of Fig. (2c).[10] The most highly connected of these (with 6 bonds) does not correspond to a realisable cluster;[14,29] it is not possible for all of the 4 rods to interact simultaneously with all of the other 3 rods via the attractive part of the interaction. Therefore, it is the diagram with 5 bonds (the middle one of Fig. (2c)) which dominates at low temperature. Five bonds means a factor of $\exp[5\epsilon/T]$. The region of integration

over which all 5 bonds are simultaneously present scales as δ^{14}. This result may be derived if we start from the B_3 integral and add an extra rod, which interacts with 2 of the existing rods. The integral over the 3 rods in B_3 yields a factor of δ^9, then restricting the orientation of the fourth rod introduces an additional factor of δ^2. The centre of mass of the fourth rod must be restricted in all 3 directions in order that it interact with 2 other rods; this gives a factor of δ^3. So, we can find the order of the diagrams in the nth virial coefficient with respect to $\exp[\epsilon/T]$ and δ by starting from diagrams in the $(n-1)$th coefficient and adding another rod such that the cluster is still realisable, i.e., that all the rods can simultaneously interact via all the bonds in the diagram. However, this quickly becomes tedious as n increases. We have found that the part of B_4 due to the attractive interactions scales as $\exp[5\epsilon/T]\delta^{14}$, and so becomes non-zero at temperatures such that both B_2 and B_3 are still at their $T = \infty$ limits. The trend seems clear, B_n starts to differ from its $T = \infty$ limit at a temperature which increases with n.

So far, we have just studied the virial coefficients of sticky cylinders. As the third virial coefficient diverges at all temperatures such that the attractive interactions influence B_2, a fluid of sticky cylinders is unstable at these temperatures, just as sticky spheres are.[14] However, the main object of our study is a polymer chain consisting of an sequence of N of these sticky cylinders. In a polymer coil the effective second virial coefficient is not that of the monomers B_2 but is B_2 renormalised by the higher coefficients, B_2^r.[1] The temperature at which the coil is ideal is the temperature at which B_2^r is zero. At low temperatures the higher virial coefficients are much larger than B_2 and so it is reasonable to expect the renormalisation to produce a renormalised B_2^r which differs substantially from the B_2 of Eq. (5). Indeed, there is no reason why the scaling of B_2^r and B_2 with δ and ϵ should be the same. Unfortunately we do not know how to carry out this renormalisation. In conclusion, at high temperatures we can approximate B_2^r by B_2 and in the coil state B_2^r is all we require. The assumption that $B_2^r \sim B_2$ near the $T = \infty$ limit is reasonable because then for $L/D \gg 1$ the higher virial coefficients are all very small. At low temperatures we have little idea of the size of B_2^r and so we are unable to construct a virial expansion of the free energy of a coil. The crossover temperature between these two regimes will be estimated in Section V.

IV. THE GLOBULAR STATE

A globule, because it is denser than a coil, has a lower entropy. This is compensated by its lower energy due to attractive interactions between the monomers of the polymer. Our rodlike monomers only attract each other when they are side-by-side and nearly parallel. Given this, it is easy to see that a monomer has the lowest energy when it is closely surrounded by 6 other monomers, all of which are nearly parallel and have their centres of mass almost in a plane. Then the monomer interacts strongly with 6 other monomers, the maximum number possible. The lowest energy state of the polymer is then just a state which allows every monomer to be surrounded in this way by 6 others. This occurs in a solid formed from layers of cylinders arranged in 2-dimensional hexagonal lattices. It is not surprising that the lowest energy is achieved in a solid but it should be noted that our monomers have to lie side-by-side to attract each other and so the energy of any isotropic phase will be much higher than that of a phase with orientational ordering. In addition the orientational ordering must be very pronounced, the angle the monomers make with the director should not be more than $\sim \delta$. The restriction that the centres of mass must be within $(1 + \delta)D$ in order for them to attract each other forces the density to be very high, roughly a fraction $1/(1 + \delta)^2$ of the density of close packing — the maximum possible density. A globule with a volume fraction of, say, 1% would necessarily have a much higher energy due to the very short range of the attractions.

As we expect a globule of such high density, a cell theory[18,30] is used to estimate its free energy. We consider a very dense layer of cylinders with their centres of mass on a 2-dimensional triangular lattice; the lattice constant is $(1 + \delta/2)D$. As the interlayer interactions are very weak in our model we do not consider the interactions between monomers in different layers. Fig. (1b) is a schematic of part of such a layer. In a cell theory calculation, the nearest neighbours of a particle are fixed at their places in a perfect lattice and the partition function q_1 of a particle trapped in the cell formed by them evaluated. So, the centres of mass of the six neighbours of the particle are fixed at positions $(1 + \delta/2)D$ away from the centre of the cell of the particle and in the xy-plane of our coordinate system and their centrelines are parallel to its z-axis. The cylinder in the cell has 5 degrees of freedom, 3 translational and 2 rotational. As our model is defined so that the orientational and translational degrees of freedom are decoupled, estimating the volume of phase space available to the rod is straightforward. The orientational degrees of freedom give a factor of $(1/2)\delta^2$, as for B_2. We approximate the volume available to the centre of mass of the rod by a hexagonal prism with its axis along the z axis. The height of the prism is $2\delta D$ and the distance from its centre to any of its points is $(1/2)\delta D$; its volume is then $0.75\sqrt{3}(\delta D)^3$. So,

$$q_1 \simeq \frac{3\sqrt{3}}{8}D^3\delta^5 \exp[3\epsilon/T] \tag{8}$$

and the free energy per monomer a is

$$a(T) = -T \ln q_1 \simeq -3\epsilon - T \ln \left[\frac{3\sqrt{3}}{8} D^3 \delta^5 \right]. \tag{9}$$

The integral over the momenta coordinates has been neglected; it is the same in all phases and so has no effect on the phase behaviour. In taking $a(T)$ to be the free energy per monomer of our polymer we have neglected the entropy associated with the number of ways in which the monomers can be connected by the spacers; this is of order unity.

V. THE COIL–GLOBULE PHASE TRANSITION

In Section II, we showed only that the when B_2 becomes negative the higher coefficients are already negative, and infinite. Now that we have an estimate of the free energy of the globule we can determine the stability of the coil with respect to the globule when B_2 becomes negative. In the limit of $\delta \to \infty$ the second term of B_2, Eq. (5), is finite if ϵ diverges as $\epsilon \to \ln \delta^{-4}$. Putting this dependence of ϵ into Eq. (9) for the free energy of a globule, results in the free energy of the globule tending to $-\infty$. Thus, for cylinders with a very short ranged, sticky, attraction the coil is unstable with respect to the globule when the (unrenormalised) interaction between a pair of monomers becomes attractive. The coil is only stable at temperatures such that B_2 equals its $T = \infty$ limit.

Now, as the free energy per particle of the coil state is constant (at high temperature) and given by Eq. (2), we can estimate the temperature of the coil–globule transition T_{cg} by equating the free energy of the globule state, Eq. (9), to that in the coil state, Eq. (2),

$$\frac{T_{cg}}{\epsilon} \simeq \frac{-3}{\ln \left[\frac{3\sqrt{3}}{8} \delta^5 \right]}. \tag{10}$$

Above T_{cg} the coil is more stable than the globule, below T_{cg} the reverse is true. At T_{cg}, the coil collapses via a strongly first order transition to form a dense globule. This is qualitatively different from the situation when the polymer is flexible, there the radius of gyration changes continuously as the temperature is varied.[2,4,7] *A posteriori* justification for the correctness of Eq. (10) is provided by the fact that it predicts a T_{cg} at which both B_2, Eq.(5), and B_3, Eq. (7), are equal to their $T = \infty$ limits. So, unless B_2^r at T_{cg} contains large contributions from higher order virial coefficients the coil is close to its $T = \infty$ limit at T_{cg} and so the free energy per monomer is close to the value of Eq. (2). Physically, large contributions from high order virial coefficients corresponds to clustering, i.e., significant numbers of monomers in the coil would be part of clusters of 4 or more monomers.[12] At equilibrium, there seems no reason for small clusters to be favoured, if the attractive interactions are strong enough to bind a few monomers into a cluster then they are strong enough to form a macroscopic cluster — the globular phase.

The temperature T_{cg} is an approximation to the temperature at which a fluid of the (unpolymerised) monomers becomes unstable with respect to a dense solid.[11,12] It is an overestimate as free monomers possess translational entropy in the fluid phase which stabilises the fluid. On the basis of our analysis here we expect a fluid of long rodlike objects with short ranged attractions to undergo a strongly first order transition to a very dense phase, when the attractions are made sufficiently strong. This appears to happen for short, ~ 50nm, lengths of DNA.[31] Wissenburg et al.[31] have observed that, on increasing the concentration of the DNA, it suddenly forms dense aggregates.

VI. CONCLUSION

The polymer never forms an ideal coil, at temperatures above T_{cg} it exists as a swollen coil and below T_{cg} it forms a crystalline globule. The coil–globule transition is strongly first order. A cell theory was used to calculate the free energy of the globular state and so to find the coil–globule transition temperature T_{cg}; the virial expansion for the free energy of our polymer having been shown to be useless at low temperatures. The coil–globule transition of a flexible polymer is second order,[5,7,32,33] the radius of gyration varies continuously with temperature. This globule is liquid-like, there is no orientational or translational ordering. Clearly, as the stiffness of the monomers is increased there is a change in the character of the coil–globule transition; this change has been observed in simulations of lattice models.[34–37] Experimentally, data is only available for highly flexible polymers, such as polystyrene[4,7,38] and DNA.[8,9], which is semiflexible The data for flexible chains seems consistent with theoretical results based on virial expansions[2,4,5,7] and with simulations of flexible chains on a lattice.[32,33] However, DNA forms dense[8,9,39,40] globules in which the DNA helices are hexagonally ordered. We have studied, using theory, a molecular model which also forms

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dense ordered globules. The major difference between our model and DNA is that DNA is semiflexible, which means that the helix bends continuously, whereas our chain consists of completely rigid monomers, which cannot bend at all, and spacers, at which the chain can bend freely. We hope to be able to incorporate the effect of continuous flexibility in future work.
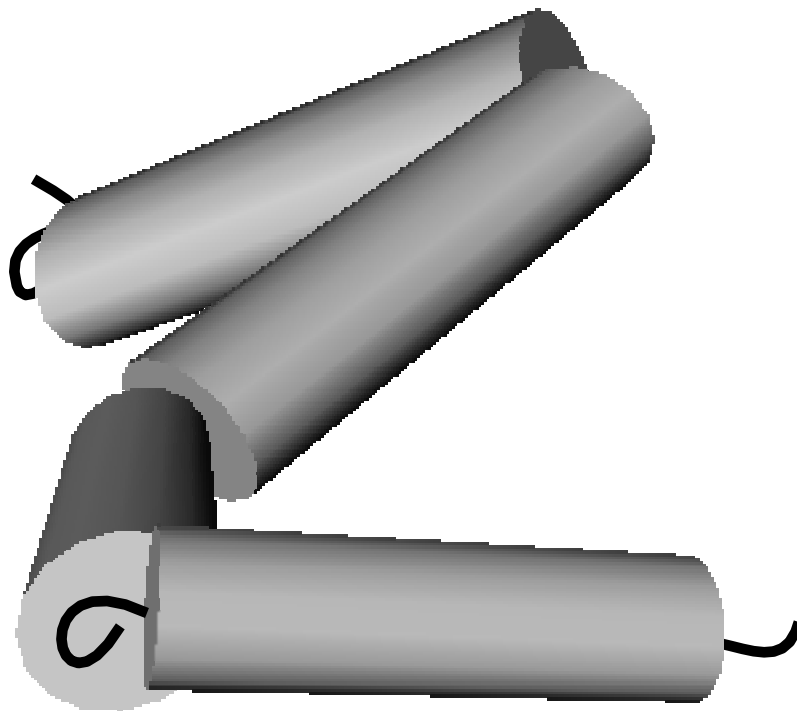
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FIG. 1.   Part of a polymer chain consisting of N rigid cylindrical monomers connected by flexible spacers; a) shows the chain in the coil state and b) in the globule state. The cylindrical monomers are shown with a diameter smaller than D in order to be able to see the hexagonal packing in the globule state. The curved black lines represent the spacers.

FIG. 2.   The diagrams for the second, a), third, b), and fourth, c), virial coefficients. The black circles represent the rods and the lines represent Mayer f functions, which are $\exp[-u/T] - 1$. A diagram with n circles is an integral over the coordinates of n rods, interacting by the Mayer f functions shown in the diagram, divided by a symmetry number.
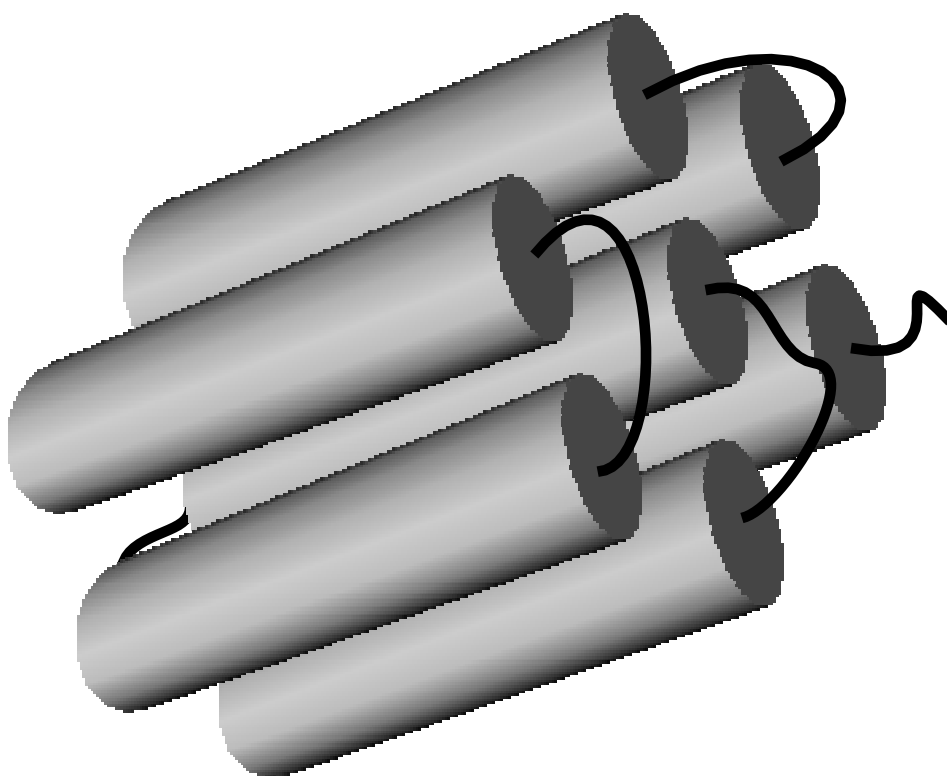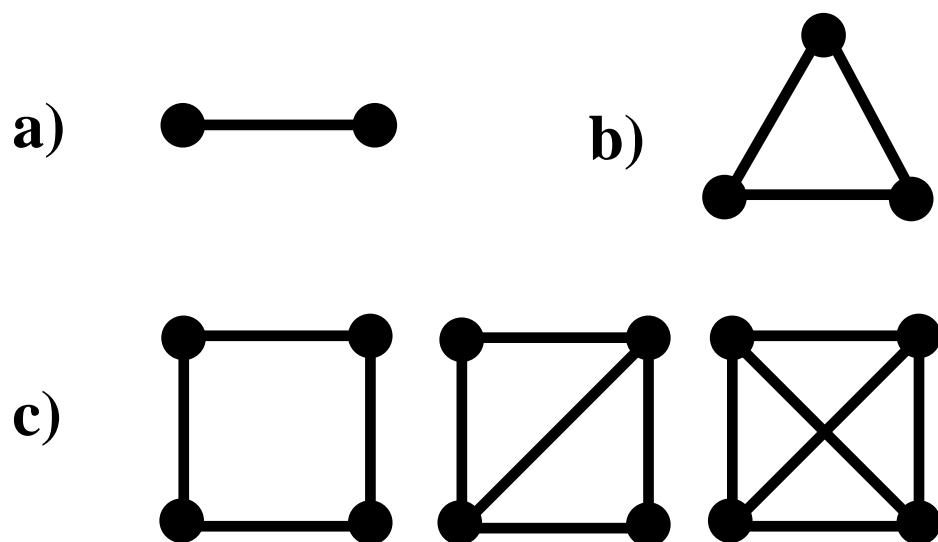
a)

b)

Fig. 1

a)

b)

c)

Fig. 2